Reduction Equilibria of Iron Oxides. I : Measurement of the Equilibrium of Reaction, Fe_3O_4 (in Wuestit) $+CO=3FeO$ (in Wuestit) $+CO_2$

Reduction Equilibria of Iron Oxides. I
Measurement of the Equilibrium of Reaction, Fe_3O_4 (in Wuestit) + CO = 3FeO (in Wuestit) + CO_2*

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I. Introduction

The following four reactions have been given, hitherto, for the reactions of iron oxides reduction by CO gas. Especially equilibrium of reactions (2) and (3) were investigated already by many authors.[1]

$$3Fe_2O_3+CO=2Fe_3O_4+CO_2 \quad (1)$$
$$Fe_3O_4+CO=3FeO+CO_2 \quad (2)$$
$$FeO+CO=Fe+CO_2 \quad (3)$$
$$Fe_3O_4+4CO=3Fe+4CO_2 \quad (4)$$

where FeO is not a chemically pure compound but a solid solution formed from FeO and Fe_3O_4, this is named wuestit. The following reaction proceeds in the wuestit,

$$Fe_3O_4(\text{in wuestit})+CO = 3FeO(\text{in wuestit})+CO_2. \quad (5)$$

No one has ever measured the equilibrium of this reaction up to this time. Wieberg[2], however, calculated the relation between CO% in gas and O_2% in wuestit at some temperatures, assuming wuestit to be a solid solution formed from FeO and O_2.

Therefore the author measured the equilibria of this reaction at the temperature range from 700°C to 1,200°C.

II. Experimental method

Fig. 1 shows the outline of experimental apparatus which consists of three parts, namely, producing and cleaning apparatus of CO and CO_2, oxidation and reduction apparatus of samples, and analytical apparatus of O_2 in wuestit by H_2.

At first 0.3~0.5 g. Fe_2O_3 was weighed in a boat and charged into the reaction tube;

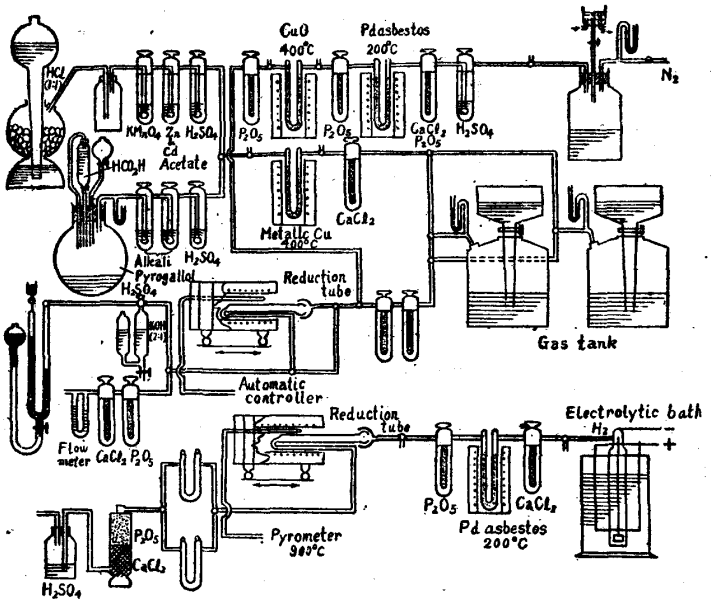

Fig. 1.

then CO-CO_2 mixed gas of a given ratio was passed through the tube at the rate of 80~100 cc./min. at a given temperature continuously. The reaction velocity between iron oxide and CO-CO_2 mixed gas was so slow that the author could not determine by gas analysis whether this system attained to equilibrium or not. Therefore the author measured the relation between residual O_2% in wuestit and experimental time and obtained the time required for equilibrium.

Ranges of ratio of CO and CO_2 in mixed gas, keeping equilibrium with wuestit at given temperatures, have been concluded from equilibrium of reactions (2) and (3).

* The 4th report of the Research Institute of Mineral Dressing and Metallurgy.

Table 1. Results of experiments.

Temp. (°C)	No. of experiments	CO(%)	CO_2(%)	CO_2/CO	Wuestit O_2(%)	N_{FeO}	$N_{Fe_3O_4}$	$N_{Fe_3O_4}/(N_{FeO})^3$	Log CO_2/CO	Note
	40	59.0	41.0	0.70	23.32	0.9305	0.0695	0.0863	−0.1549	←
	42	55.8	44.2	0.79	23.61	0.9071	0.0929	0.1245	−0.1024	→
	44	50.5	49.5	0.98	23.55	0.9210	0.0790	0.1010	−0.0088	→
	47	42.3	57.7	1.36	23.83	0.8906	0.1094	0.1548	0.1335	→
	50	40.3	59.7	1.48	24.02	0.8702	0.1298	0.1969	0.1703	←
700	51	48.8	51.2	1.05	23.82	0.8888	0.1112	0.1583	0.0212	←
	52	45.0	55.0	1.22	23.82	0.8888	0.1112	0.1583	0.0864	←
	FeO-Fe (R.Schenck)	60.1	39.9	0.66	23.06	0.9498	0.0502	0.0585	−0.1805	
	Fe_3O_4-FeO (R.Schenck)	35.3	64.7	1.83	24.35	0.8367	0.1633	0.2788	0.2625	
	30	64.1	35.9	0.56	23.12	0.9455	0.0545	0.0645	−0.2518	←
	28	57.2	42.8	0.75	23.49	0.9170	0.0830	0.1076	−0.1249	→
	32	53.6	46.6	0.87	23.54	0.9120	0.0870	0.1143	−0.0605	→
	31	52.5	47.5	0.90	23.63	0.9054	0.0946	0.1274	−0.0458	→
	29	50.3	49.7	0.99	23.55	0.9122	0.0873	0.1156	−0.0044	←
	33	37.5	62.5	1.67	23.90	0.8815	0.1185	0.1730	0.2227	→
800	36	36.6	63.4	1.73	23.85	0.8861	0.1139	0.1637	0.2381	→
	34	30.1	69.9	2.32	24.24	0.8482	0.1518	0.2488	0.3655	→
	37	40.4	59.6	1.48	23.94	0.8778	0.1222	0.1806	0.1703	←
	FeO-Fe (R.Schenck)	65.2	34.8	0.53	22.95	0.9575	0.0425	0.0484	−0.2757	
	Fe_3O_4-FeO (R.Schenck)	27.5	72.5	2.64	24.35	0.8367	0.1633	0.2788	0.4216	
	2	67.4	32.6	0.48	22.98	0.9555	0.0445	0.051	−0.3188	←
	4	66.6	33.4	0.50	23.00	0.9541	0.0459	0.053	−0.3019	→
	5	60.5	39.5	0.65	23.38	0.9254	0.0741	0.093	−0.1871	←
	6	50.6	49.4	0.98	23.55	0.9133	0.0887	0.117	−0.0088	→
	13	45.7	54.3	1.19	23.74	0.8963	0.1038	0.143	0.0756	→
	7	34.7	65.3	1.88	24.09	0.8624	0.1376	0.214	0.2742	←
900	15	34.6	65.4	1.89	24.02	0.8702	0.1298	0.196	0.2765	→
	12	31.1	68.9	2.22	24.23	0.8493	0.1507	0.246	0.3464	←
	9	24.3	75.7	3.12	24.37	0.8344	0.1656	0.285	0.4942	→
	FeO-Fe (R.Schenck)	68.7	31.3	0.45	22.84	0.9679	0.0321	0.0354	−0.3468	
	Fe_3O_4-FeO (R.Schenck)	22.1	77.9	1.09	24.51	0.8325	0.1675	0.290	0.5465	
	17	39.5	60.5	1.53	24.13	0.8594	0.1405	0.2213	0.1817	←
	22	69.0	31.0	0.45	23.07	0.9491	0.0506	0.0595	−0.3408	←
	25	47.9	52.1	1.09	23.77	0.8933	0.1067	0.1496	0.0374	←
	54	65.6	34.4	0.52	23.52	0.9146	0.0854	0.1116	−0.2807	←
	55	67.5	32.5	0.61	23.32	0.9305	0.0695	0.0685	−0.2170	←
	56	54.0	46.0	0.85	23.58	0.9097	0.0903	0.1199	−0.0716	→
	57	55.1	44.9	0.82	23.64	0.9045	0.0955	0.1290	−0.0894	→
1000	58	41.1	58.9	1.43	23.95	0.8768	0.1232	0.1827	0.1562	→
	59	30.0	70.0	2.33	24.11	0.8613	0.1397	0.2186	0.3680	→
	77	30.1	69.9	2.32	24.16	0.8564	0.1436	0.2286	0.3655	→
	78	31.2	68.8	2.21	24.29	0.8446	0.1554	0.2579	0.3444	←
	FeO-Fe (R.Schenck)	72.0	28.0	0.39	22.79	0.9683	0.0317	0.0348	−0.4089	
	Fe_3O_4-FeO (R.Schenck)	16.7	83.3	4.95	24.62	0.8062	0.1938	0.3698	0.6972	
	60	70.6	29.4	0.416	22.92	0.9596	0.0404	0.0457	−0.3809	←
	62	70.3	29.7	0.422	23.15	0.9433	0.0562	0.0670	−0.3747	←
	64	61.5	38.5	0.626	23.30	0.9320	0.0680	0.0840	−0.2034	←
	65	52.5	47.5	0.905	23.63	0.9078	0.0922	0.1232	−0.0434	→
	67	58.3	41.7	0.715	23.49	0.9170	0.0830	0.1076	−0.1457	→
	68	44.0	56.0	1.273	24.10	0.8624	0.1376	0.2145	0.1048	←
	71	40.1	59.9	1.494	24.07	0.8653	0.1347	0.2079	0.1744	→
1100	69	15.1	84.9	5.622	24.71	0.7953	0.2047	0.4070	0.7499	←
	72	29.9	71.1	2.378	24.24	0.8482	0.1518	0.2488	0.3762	→
	74	29.2	71.8	2.459	24.33	0.8387	0.1613	0.2734	0.3908	←
	76	30.9	69.1	2.236	24.30	0.8420	0.1580	0.2647	0.3495	←
	FeO-Fe (R.Schenck)	74.5	25.5	0.342	22.67	0.9786	0.0214	0.0228	−0.4660	
	Fe_3O_4-FeO (R.Schenck)	13.4	86.6	6.462	24.78	0.7806	0.2134	0.4867	0.8104	

Table 1. (Continued)

Temp. (°C)	No. of experiments	CO(%)	CO_2(%)	CO_2/CO	Wuestit O_2(%)	N_{FeO}	$N_{Fe_3O_4}$	$N_{Fe_3O_4}/(N_{FeO})^3$	Log CO_2/CO	Note
	85	72.6	27.4	0.377	22.90	0.9013	0.0387	0.0436	−0.4237	←
	92	64.0	38.0	0.612	23.07	0.9491	0.0509	0.0595	−0.2136	←
	94	70.9	29.1	0.410	23.10	0.9469	0.0531	0.0625	−0.3872	←
	95	46.4	53.6	1.157	24.01	0.8712	0.1288	0.1947	0.0633	←
	98	52.2	47.8	0.915	23.46	0.9194	0.0806	0.1037	−0.0386	→
1200	102	43.9	56.1	1.210	23.99	0.8731	0.1269	0.1907	0.1071	→
	105	30.7	69.3	2.255	24.50	0.8201	0.1799	0.3261	0.3532	←
	FeO-Fe (R.Schenck)	75.4	24.6	0.33	22.63	0.9787	0.0213	0.0227	−0.4815	
	Fe_3O_4-FeO (R.Schenck)	11.2	88.3	7.89	24.80	0.7842	0.2158	0.4474	0.8971	

III. Results of experiment

The results of all measurements are given in Table 1. Now if we plot CO % in gas against O_2% in wuestit at a definite temperature, a curve is obtained as shown in Fig. 2. This shows an example at 900°C. In Fig. 2 ⊸ expresses the concentration of O_2 when the system is made to equilibrium by reducing with CO-CO_2 mixed gas at the definite ratio from the beginning and ⊸ means that of O_2 made in equilibrium by reducing at the beginning with CO rich mixed gas whose ratio is far closer to the gas ratio in equilibrium with FeO-Fe, then by oxidizing with the mixed gas of desired ratio.

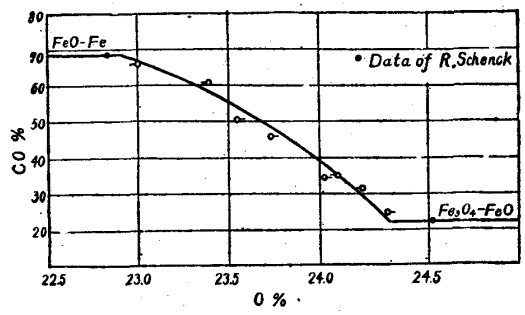

Fig. 2.

Horizontal lines of upper and lower limits show equilibrium gas composition in reactions (2) and (3).

Now N_{FeO} and $N_{Fe_3O_4}$ denote molar fractions of FeO and Fe_3O_4 in wuestit respectively. Assuming that wuestit is an ideal solid solution, then we may obtain a relation in a straight line by plotting CO_2/CO against $N_{Fe_3O_4}/(N_{FeO})^3$ but the results of experiments, for example in Fig. 3 at 900°C, are shown by the following empirical formula.

$$\frac{CO_2}{CO} = ae^{b\frac{N_{Fe_3O_4}}{(N_{FeO})^3}}, \qquad (6)$$

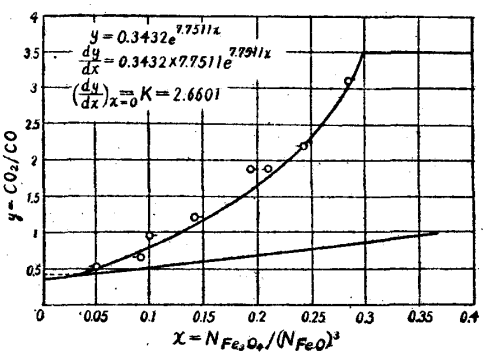

Fig. 3.

where a and b are constants at a definite temperature respectively. Calculating a and b in the equation (6) from the data of Table 1 at given temperatures, we obtain empirical formulas in Table 2.

Table 2. Relations between CO_2/CO and $N_{Fe_3O_4}/(N_{FeO})^3$ at given temperatures.

Temp. (°C)	Empirical formulas
700	$y=0.3490e^{8.5420x}$
800	$y=0.3445e^{8.3280x}$
900	$y=0.3432e^{7.7511x}$
1000	$y=0.3351e^{7.4971x}$
1100	$y=0.3325e^{7.7297x}$
1200	$y=0.3152e^{7.2069x}$

where $y=CO_2/CO$, $x=N_{Fe_3O_4}/(N_{FeO})^3$

a_{FeO} and $a_{Fe_3O_4}$ denote the activities of FeO and Fe_3O_4, γ_{FeO} and $\gamma_{Fe_3O_4}$ the activity coefficients of FeO and Fe_3O_4 respectively, and as a standard state γ_{FeO} and $\gamma_{Fe_3O_4}$ are chosen as unity where N_{FeO} is infinitely

dilute. In such a case activities coincide with molar fractions where $N_{Fe_3O_4}$ is infinitely dilute and the equilibrium constant can be obtained from the inclination of tangent line when $N_{Fe_3O_4}$ is zero at given temperatures as shown in Fig. 3.

Thus the relation between CO_2/CO and $a_{Fe_3O_4}/(a_{FeO})^3$ becomes as follows:

$$\frac{CO_2}{CO} = a + K\frac{(a_{FeO})^3}{a_{Fe_3O_4}} \qquad (7)$$

Hence, $K=(CO_2/CO-a)(a_{FeO})^3/a_{Fe_3O_4}$.

If we calculate values of K at given temperatures from empirical formulas in Table 2, we can obtain the data in Table 3.

Table 3. Values of K and $\log K$ at given temperatures.

Temp. (°C)	K	$\log K$
700	2.9812	0.4742
800	2.8689	0.4578
900	2.6601	0.4249
1000	2.5123	0.4000
1100	2.4205	0.3838
1200	2.2716	0.3564

Using the data in Table 3, temperature functions of $\log K$ and $\Delta F°$ are calculated.

$$\log K = 433.0248/T + 0.00635\log T + 0.00004487T - 0.0175. \qquad (8)$$

$$\Delta F° = -1982.691 - 0.0290T\log T - 2.0524\cdot 10^{-4}T + 0.801T. \qquad (9)$$

IV. Relation between CO% in gas and O_2% in wuestit

CO% in gas, when it maintains an equilibrium with wuestit of a given O_2% at a given temperature, can be calculated from empirical formulas in Table 2. Assuming O_2% in wuestit are 23.0, 23.5, 24, and 24.5% respectively, and calculating CO% in gas under the condition of equilibrium with these wuestits, we can draw isooxygen-concentration lines in the wuestit field on the equilibrium diagram of reduction of iron oxides by CO as shown in Fig. 4. In Fig. 4, graphically calculated values from isothermal reduction equilibrium diagram of iron oxides, reported by R. Schenck and Matsubara[1] and thermodynamically calculated values by Wieberg[2] were shown for comparison.

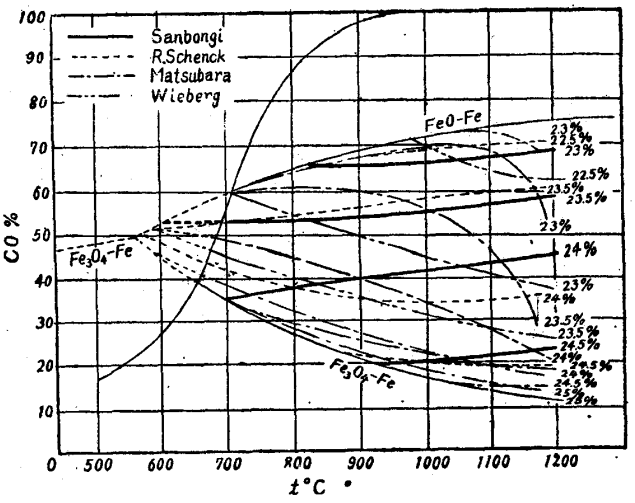

Fig. 4.

V. Equilibrium of the reaction, Fe_3O_4 (in wuestit)$+H_2=3FeO$ (in wuestit)$+H_2O$

From the temperature functions of equilibrium constant of equation (8) and of water gas reaction, we can calculate temperature functions of $\log K$ and $\Delta F°$ of this reaction, because the temperature function of $\log K$ of water gas reaction has been reported already by Neumann and Koehler.[3]

$$CO_2+H_2=CO+H_2O$$

$$\log K = \frac{p_{CO}p_{H_2O}}{p_{CO_2}p_{H_2}} = -2190/T - 0.201\log T - 0.000393T + 5.46\cdot 10^{-8}T^2 + 2.979. \qquad (10)$$

From equations (8) and (10),

$$Fe_3O_4(\text{in wuestit})+H_2 = 3FeO\ (\text{in wuestit})+H_2O$$

$$\log K = \left(\frac{p_{H_2O}}{p_{H_2}} - a'\right)\frac{(a_{FeO})^3}{a_{Fe_3O_4}} = -1756.975/T - 0.19465\log T - 0.000348T + 5.46\cdot 10^{-8}T + 2.9615. \qquad (11)$$

Furthermore,

$$\Delta F° = 8044.66 + 0.8912T\log T + 0.001593T - 24.9795\cdot 10^{-8}T^3 - 13.5479T. \qquad (12)$$

Relations between H_2O/H_2 and $N_{Fe_3O_4}/(N_{FeO})^3$ at given temperatures are expressed by the following formula,

$$\frac{H_2O}{H_2} = a'e^{b'}\frac{N_{Fe_3O_4}}{(N_{FeO})^3}, \qquad (13)$$

where a' and b' are constants at given temperatures respectively. Calculating a' from values of a in Table 1 and equilibrium constant of water gas reaction and b' from

$b'=\frac{K}{a'}$ at given temperatures, we obtain empirical formulas in Table 4, respectively. H_2% in gas when it maintains an equilibrium with wuestit of a given O_2% at each temperatures, can be calculated from empirical formulas in Table 4. Assuming O_2% in wuestit are 23.0, 23.5, 24 and 24.5 % respectively and calculating H_2 % in gas which maintains equilibrium with these wuestits, wecan draw isooxygen-concentration lines in the wuestit field of equilibrium diagram of iron oxides reduction by H_2, as in the case of Fig. 4.

Table 4. Relation between H_2O/H_2 and $N_{Fe_3O_4}/(N_{FeO})^3$ at given temperatures.

Temp. (°C)	Empirical formulas
700	$y=0.2192e^{8.7591x}$
800	$y=0.3213e^{8.3193x}$
900	$y=0.4410e^{7.8185x}$
1000	$y=0.5560e^{7.4064x}$
1100	$y=0.6880e^{7.3202x}$
1200	$y=0.7817e^{7.2930x}$

where $x=\frac{N_{Fe_3O_4}}{(N_{FeO})^3}$, $y=\frac{H_2O}{H_2}$.

Fig. 5 shows these isooxygen-concentration lines calculated by the author and the dotted lines are those of Wieberg.[2] Equilibrium lines of FeO-Fe and Fe_3O_4-FeO, occupying upper and lower limits on this figure, were drawn from Eastman and Evan's data[1], which were reported as the best values.

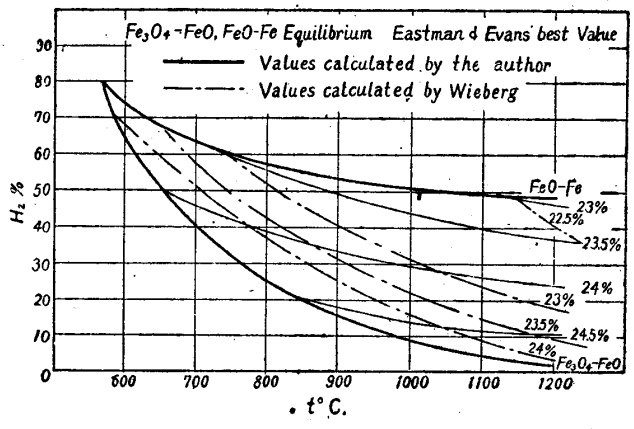

Fig. 5.

VI. Equilibrium of the reaction, Fe_3O_4(in wuestit)$=3FeO$ (in wuestit)$+1/2O_2$

From temperature functions of equilibrium constant of equation (8) and dissociation of CO_2 which has been reported by Wartenberg[4], we can calculate temperature functions of dissociation constants and $\Delta F°$ of this reaction.

$$CO_2=\frac{1}{2}O_2+CO$$

$$\log D_{CO_2}=\frac{P_{CO}P_{CO_2}^{1/2}}{P_{CO_2}}=-14750/T+1.375\log T-0.6075\cdot10^3T+0.675\cdot10^{-7}T+1.10. \quad (14)$$

From equations (8) and (14),

$$Fe_3O_4(\text{in wuestit})=3FeO(\text{in wuestit})+\frac{1}{2}O_2$$

$$\log D=(P_{O_2}^{1/2}-p_{O_2}^{1/2})\frac{(a_{FeO})^3}{a_{Fe_3O_4}}=-14317/T+1.3814\log T-0.000563T+0.675\cdot10^{-7}T^2+1.0825, \quad (15)$$

where oxygen pressure of wuestit is given by P_{O_2} and oxygen pressure of pure FeO is shown by p_{O_2} which is a constant at a given temperature. From equation (15)

$$\Delta F°=65553.25-6.3248\log T+0.002576T-3.0906\cdot10^{-7}T^2-4.9564. \quad (16)$$

Relations between p_{O_2} and $N_{Fe_3O_4}/(N_{FeO})^3$ at given temperatures are expressed by the following formula,

$$P_{O_2}^{1/2}=p_{O_2}^{1/2}e^b\frac{N_{Fe_3O_4}}{(N_{FeO})^3}, \quad (17)$$

where b_1 is a constant at a given temperature.

Calculating $P_{O_2}^{1/2}$ from values of a in Table 1 and dissociation constant of CO_2 and b_1 from $b_1=D/p_{O_2}^{1/2}$ at given temperatures, we obtain empirical formulas in Table 5 respectively.

Calculating oxygen pressure in wuestits, when oxygen concentrations are 23, 23.5, 24 and 24.5 % respectively, from empirical formulas in Table 5 at given temperatures and drawing isooxygen-concentration lines in the wuestit field on the dissociation equilibrium diagram of iron oxides, we obtain Fig. 6.

Curves of upper and lower limits in Fig. 6 show relation between dissociation pressures

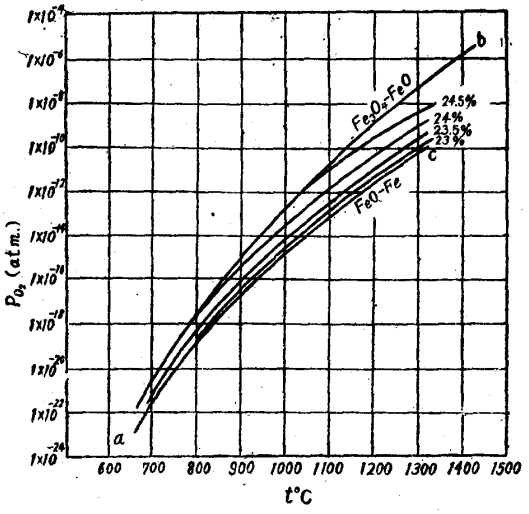

Fig. 6.

of FeO and Fe_3O_4 and temperature respectively. Temperature functions of these dissociation constants are calculated from H. Schenck's data on the reduction equilibrium of FeO-Fe and Fe_3O_4-FeO with CO and dissociation equilibria of CO_2 by Wartenberg[4] respectively.

They are expressed by the following equations:

$$Fe_3O_4 = 3FeO + \frac{1}{2}O_2$$

$$\log P_{O_2}(\text{atm.}) = -32246/T + 2.068\log T - 0.395\cdot 10^{-3}T + 1.35\cdot 10^{-7}T^2 + 6.806 \quad (18)$$

$$FeO = Fe + \frac{1}{2}O_2$$

$$\log P_{O_2}(\text{atm.}) = -28738/T - 1.47\log T - 0.425\cdot 10^{-3}T + 1.35\cdot 10^{-7}T^2 + 12.914. \quad (19)$$

Table 5. Relations between CO_2/CO and $N_{Fe_3O_4}/(N_{FeO})^3$ at given temperatures.

Temp. (°C)	$P_{O_2}^{1/2} = p_{O_2}^{1/2} e^{bN_{Fe_3O_4}/(N_{FeO})^3}$
700	$P_{O_2}^{1/2} = 0.1162\times 10e^{8.8592x}$
800	〃 $= 0.3045\times 10e^{8.2463x}$
900	〃 $= 0.4588\times 10e^{7.7300x}$
1000	〃 $= 0.4400\times 10e^{7.4288x}$
1100	〃 $= 0.3066\times 10e^{7.2055x}$
1200	〃 $= 0.1560\times 10e^{7.3067x}$

where $x = N_{Fe_3O_4}/(N_{FeO})^3$

VII. Determination of activities of FeO and Fe_3O_4 in wuestit

$$\frac{CO_2}{CO} = ae^{bN_{Fe_3O_4}/(N_{FeO})^3} \quad (6)$$

$$\frac{CO_2}{CO} = a + K\frac{a_{Fe_3O_4}}{(a_{FeO})^3}. \quad (7)$$

Eliminating CO_2/CO from both equations,

$$\frac{a_{Fe_3O_4}}{(a_{FeO})^3} = \frac{a}{K}\left(e^{b\frac{N_{Fe_3O_4}}{(N_{FeO})^3}} - 1\right)$$

$$\frac{\gamma_{Fe_3O_4}}{(\gamma_{FeO})^3} = \frac{\frac{K}{a}\left(e^{b\frac{N_{Fe_3O_4}}{(N_{FeO})^3}} - 1\right)}{N_{Fe_3O_4}/(N_{FeO})^3}, \quad (20)$$

and for the relation between γ_{FeO} and $\gamma_{Fe_3O_4}$ the following equation is given:

$$d\log\gamma_{FeO} = -\frac{N_{Fe_3O_4}}{(N_{FeO})^3}\cdot d\log\gamma_{Fe_3O_4}. \quad (21)$$

Furthermore,

$$N_{Fe_3O_4} + N_{FeO} = 1 \quad (22)$$

Solving equations (21), (22), and (23), for FeO and substituting the condition $\gamma_{FeO}=1$ when $N_{Fe_3O_4}=0$.

$$\log\gamma_{FeO} = -\int_0^{N_{FeO}} \frac{N_{Fe_3O_4}}{N_{FeO}+3N_{Fe_3O_4}} \cdot d\log\frac{e^{b\frac{N_{Fe_3O_4}}{(N_{FeO})^3}} - 1)}{N_{Fe_3O_4}/(N_{FeO})^3}. \quad (23)$$

If we integrate graphically by plotting $N_{Fe_3O_4}/N_{FeO}+3N_{Fe_3O_4}$ as ordinates against $\log\,(e^{bN_{FeO}/(N_{Fe_3O_4})^3}-1)/N_{Fe_3O_4}/(N_{FeO})^3$ as abscissae, we can obtain values of γ_{FeO} and a_{FeO} by measuring whole areas under the curve from the origin to the given $N_{Fe_3O_4}/N_{FeO}+3N_{Fe_3O_4}$ corresponding to the given $N_{Fe_3O_4}$. Then, substituting values of γ_{FeO} in equation (20), we can obtain values of $\gamma_{Fe_3O_4}$ and a_{FeO}.

When we calculate values of a_{FeO} and $a_{Fe_3O_4}$ corresponding to some values of $N_{Fe_3O_4}$, ranging from zero to saturation, at given temperatures by these methods, we obtain data in Table 6. Plotting a_{FeO} and $a_{Fe_3O_4}$ against N_{FeO}, Fig. 7 *can be obtained.

* In this figure, dotted lines, give relations between $a_{Fe_3O_4}$ and N_{FeO} at each temperature choosing such a standard state as the activity of pure Fe_3O_4 is unity.

Table 6. a_{FeO}, $a_{Fe_3O_4}$, γ_{FeO}, $\gamma_{Fe_3O_4}$ at several temperatures.

Temp. (°C)	$N_{Fe_3O_4}$	N_{FeO}	γ_{FeO}	a_{FeO}	$\gamma_{Fe_3O_4}$	$a_{Fe_3O_4}$	$a_{Fe_3O_4}$ (pure Fe_3O_4=1)
700	0.01	0.99	0.9994	0.9894	1.0430	0.0104	0.0389
	0.03	0.97	0.9976	0.9677	1.1463	0.0344	0.1286
	0.05	0.95	0.9930	0.9434	1.2700	0.0635	0.2373
	0.07	0.93	0.9850	0.9161	1.6828	0.1178	0.4402
	0.1	0.90	0.9664	0.8698	1.7574	0.1757	0.6566
	0.1271 (Fe_3O_4 sat.)	0.8729	0.9415	0.8218	2.1054	0.2676	1
800	0.01	0.99	0.9996	0.9896	1.0481	0.0105	0.0261
	0.03	0.97	0.9980	0.9681	1.1408	0.0342	0.0849
	0.05	0.95	0.9934	0.9437	1.2617	0.0631	0.1566
	0.07	0.93	0.9856	0.9175	1.4058	0.0984	0.2442
	0.1	0.90	0.9684	0.8716	1.6969	0.1697	0.4212
	0.15	0.85	0.9180	0.7803	2.5277	0.3792	0.9412
	0.1537 (Fe_3O_4 sat.)	0.8463	0.9136	0.7732	2.6216	0.4029	1
900	0.01	0.99	0.9997	0.9897	1.0378	0.0104	0.0213
	0.03	0.97	0.9980	0.9681	1.1307	0.0339	0.0696
	0.05	0.95	0.9940	0.9443	1.2395	0.0620	0.1273
	0.07	0.93	0.9872	0.9181	1.3722	0.0961	0.1972
	0.1	0.90	0.9710	0.8748	1.6301	0.1630	0.3346
	0.15	0.85	0.9204	0.7823	2.3207	0.3481	0.7145
	0.1735 (Fe_3O_4 sat.)	0.8265	0.8798	0.7272	2.8080	0.4872	1
1000	0.01	0.99	0.9997	0.9897	1.0344	0.0103	0.0169
	0.03	0.97	0.9982	0.9683	1.1257	0.0338	0.0555
	0.05	0.95	0.9942	0.9445	1.2308	0.0615	0.1010
	1.07	0.93	0.9882	0.9190	1.3612	0.0953	0.1565
	0.1	0.90	0.9718	0.8746	1.5992	0.1599	0.2626
	0.15	0.85	0.9232	0.7847	2.2505	0.3376	0.5545
	0.1903 (Fe_3O_4 sat.)	0.8097	0.8575	0.6943	3.1992	0.6088	1
1100	0.01	0.99	0.9997	0.9897	1.0396	0.0104	0.0143
	0.03	0.97	0.9982	0.9683	1.1229	0.0337	0.0465
	0.05	0.95	0.9947	0.9450	1.2266	0.0613	0.0845
	0.07	0.93	0.9890	0.9198	1.3501	0.0945	0.1303
	0.1	0.90	0.9736	0.8762	1.5854	0.1585	0.2186
	0.15	0.85	0.9268	0.7878	2.2025	0.3304	0.4556
	0.2042 (Fe_3O_4 sat.)	0.7958	0.8334	0.6632	3.5515	0.7252	1
1200	0.01	0.99	0.9997	0.9897	1.0360	0.0104	0.0123
	0.03	0.97	0.9982	0.9683	1.1209	0.0336	0.0397
	0.05	0.95	0.9947	0.9450	1.2241	0.0612	0.0723
	0.07	0.93	0.9893	0.9200	1.3471	0.0943	0.1114
	0.1	0.90	0.9742	0.8769	1.5778	0.1578	0.1863
	0.15	0.85	0.9392	0.7983	2.2654	0.3398	0.4013
	0.20	0.8	0.8449	0.6859	3.3601	0.6720	0.7936
	0.2154 (Fe_3O_4 sat.)	0.7846	0.8090	0.6347	3.9315	0.8468	1

VIII. Determination of $\Delta\bar{F}$, $\Delta\bar{F}_{FeO}$ and $\bar{F}_{Fe_3O_4}$ of wuestit formation

If $\bar{F}_1$, and a_1 denote partial molar free energy and activity of a component in a solution respectively, then the relation between F_1, and a_1 becomes as follows:

$$\bar{F}_1 = RT\ln a_1 .$$

Therefore in wuestit,

$$\left.\begin{aligned} \Delta\bar{F}_{FeO} &= RT\ln a_{FeO} \\ &= 4.5787T\log a_{FeO} \\ \Delta\bar{F}_{Fe_3O_4} &= RT\ln a_{Fe_3O_4} \\ &= 4.5787T\log a_{Fe_3O_4} \end{aligned}\right\} \quad (24)$$

When FeO and Fe_3O_4 are pure substances and standard a_{FeO} and $a_{Fe_3O_4}$ are at unity, the change of total molar free energy of wuestit formation from FeO and Fe_3O_4 is given as follows:

$$\Delta F_1 = N_{FeO}\Delta\bar{F}_{FeO} + N_{Fe_3O_4}\Delta\bar{F}_{Fe_3O_4}. \quad (25)$$

Fig. 8 shows relations between calculated

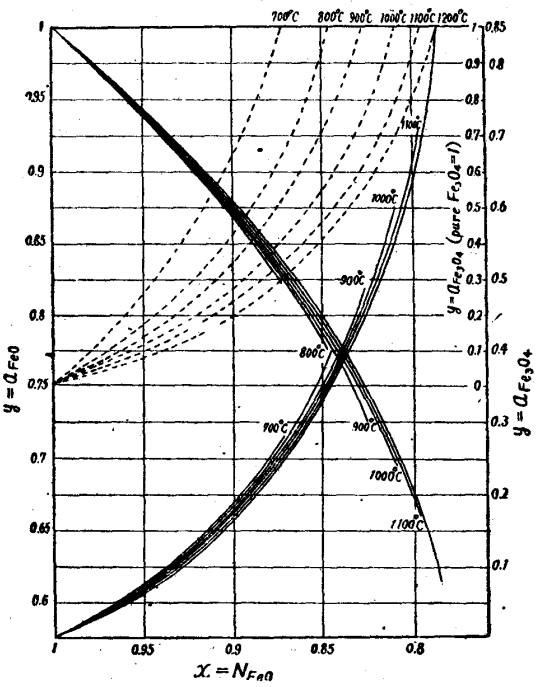

Fig. 7.

values of $\Delta\bar{F}_{FeO}$, $\Delta\bar{F}_{Fe_3O_4}$ and $\bar{F}_T$ from equations (24), (25) and N_{FeO} in wuestit at given temperatures.

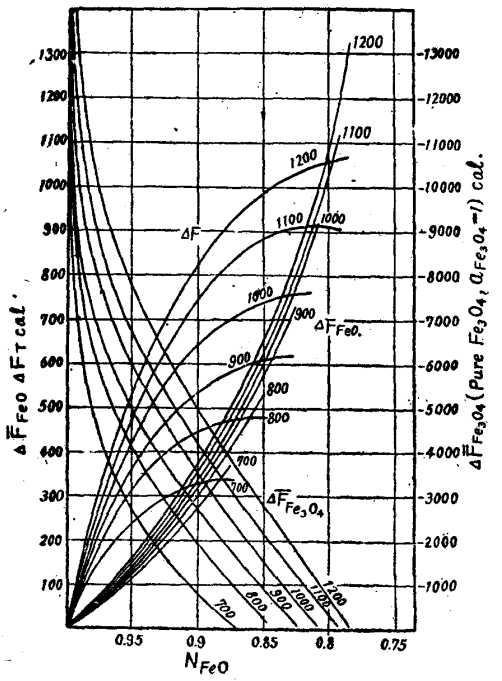

Fig. 8.

IX. Determination of ΔL, $\bar{L}_{FeO}$ and $\bar{L}_{Fe_3O_4}$ of wuestit formation

Putting relative partial molar heat content of a component in a solution at $\bar{L}_1$, then the following relation is obtained thermodynamically,

$$\frac{d\ln a_1}{dT} = -\frac{\bar{L}_1}{RT^2}.$$

For FeO in wuestit,

$$\frac{d\ln a_{FeO}}{dT} = -\frac{\bar{L}_{FeO}}{RT^2}.$$

Hence,

$$4.5787T^2\frac{d\log a_{FeO}}{dT} = -\bar{L}_{FeO}. \quad (26)$$

From experimental results, plotting a_{FeO} against temperature at a given value of $N_{Fe_3O_4}$, we get a relation in a nearly straight line so that from the inclination of this straight line, we can obtain value of $d\log a_{FeO}/dT$ and that of $\bar{L}_{FeO}$ from equation (26).

Furthermore for the relation between $\bar{L}_{FeO}$ and $\bar{L}_{Fe_3O_4}$, the following equation is obtained at a given temperature.

$$N_{FeO}d\bar{L}_{FeO} + N_{Fe_3O_4}d\bar{L}_{Fe_3O_4} = 0.$$

Hence,

$$\int d\bar{L}_{Fe_3O_4} = -\int\frac{N_{FeO}}{N_{Fe_3O_4}}d\bar{L}_{FeO} \quad (27)$$

From the equation (27), plotting the values of $\bar{L}_{FeO}$ as abcissae against those of $N_{FeO}/N_{Fe_3O_4}$ as ordinates, the area under the curve from a certain point to $N_{FeO}/N_{Fe_3O_4}=0$ gives immediately the value of $\bar{L}_{Fe_3O_4}$ at that point.

From $\bar{L}_{FeO}$ and $\bar{L}_{Fe_3O_4}$ of wuestit of a certain composition, relative molar heat content indicated by L, is calculated as follows:

$$L = N_{FeO}\bar{L}_{FeO} + N_{Fe_3O_4}\bar{L}_{Fe_3O_4}. \quad (28)$$

When one mol of wuestit is formed from n_1 mol of FeO and n_2 mol of Fe_3O_4, change of heat content are calculated by the following equation,

$$\Delta H = \Delta L = L - N_{Fe_3O_4}\bar{L}_{Fe_3O_4}(s), \quad (29)$$

where $\bar{L}_{Fe_3O_4}(s)$ means relative partial molar heat content of pure Fe_3O_4 and is obtained from equation (27) by means of extrapolation of the curve $N_{FeO}/N_{Fe_3O_4}=0$ and graphical calculation of the whole area at given temperatures.

Fig. 9 gives relations between values of ΔL, $\bar{L}_{Fe_3O_4}$, $\bar{L}_{FeO}$ and N_{FeO} calculated by these methods at given temperatures.

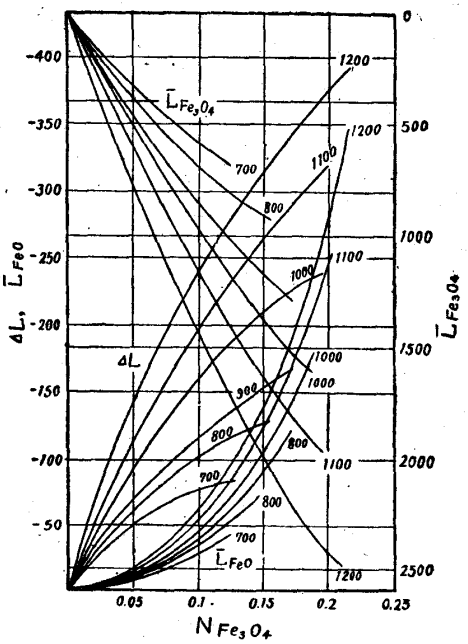

Fig. 9.

X. Determination of ΔS, $\Delta\bar{S}_{FeO}$ and $\Delta\bar{S}_{Fe_3O_4}$ of wuestit formation

Change of partial molar entropies of FeO and Fe_3O_4 in wuestit, expressed by $\Delta\bar{S}_{FeO}$ and $\Delta\bar{S}_{Fe_3O_4}$ respectively, are given as follows:

$$\left.\begin{aligned}\Delta\bar{S}_{FeO} &= \frac{(\Delta\bar{F}_{FeO}-\bar{L}_{FeO})}{T}\\ \Delta\bar{S}_{Fe_3O_4} &= \frac{(\Delta\bar{F}_{Fe_3O_4}-\bar{L}_{Fe_3O_4})}{T}\end{aligned}\right\} \qquad (30)$$

where it is necessary that both $\Delta\bar{F}$ and $\Delta\bar{L}$ are at such a standard state as $N_{Fe_3O_4}$ is zero.

When we obtain values of $\Delta\bar{S}_{FeO}$ and $\Delta\bar{S}_{Fe_3O_4}$ from equation (30), changes of total molar entropies of wuestit formation are calculated as follows:

$$\Delta S = N_{FeO}.\Delta\bar{S}_{FeO} + N_{Fe_3O_4}.\Delta\bar{S}_{Fe_3O_4} - N_{Fe_3O_4}\Delta\bar{S}_{Fe_3O_4}(s), \qquad (31)$$

where $\Delta\bar{S}_{Fe_3O_4}(s)$ means change of partial molar entropy of pure Fe_3O_4. Fig. 10 gives relation between calculated values of ΔS, $\Delta\bar{S}_{FeO}$, $\Delta\bar{S}_{Fe_3O_4}$ and N_{FeO} at given temperatures.

Summary

The author measured the equilibrium of the following reaction at the temperature range from 700°C to 1.200°C,

$$Fe_3O_4(\text{in wuestit}) + CO = 3FeO(\text{in wuestit}) + CO_2$$

According to experimental results, wuestit can not be recognized as an ideal solution. Consequently considering the activities of FeO and Fe_3O_4 in wuestit, the author obtained the equilibrium constant of the reaction (5) at given temperatures and temperature function of log K.

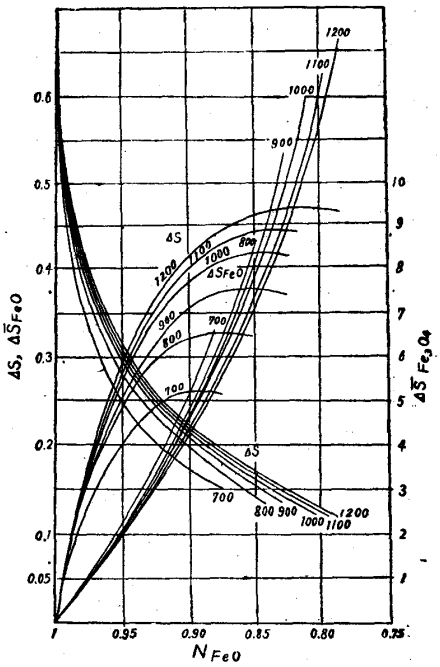

Fig. 10.

Then, from the equilibrium constant of the reaction (5) and the equilibrium constant of water gas reaction or the dissociation constant of CO_2, the author calculated the equilibrium between wuestit and H_2O-H_2 mixed gas and dissociation pressure of wuestit.

Furthermore the author calculated activities of a_{FeO} and $a_{Fe_3O_4}$ in wuestits with several O_2 concentrations at given temperatures from experimental data, and performed some thermodynamical calculations.

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